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UNITED STATES PATENT APPLICATION

OF

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FOR

DYE COMPOSITION CONTAINING 1,8-BIS(2,5-DIAMINOPHENOXY)-3,5-DIOXAOCTANE, AN ADDITIONAL OXIDATION BASE AND A COUPLER, AND DYEING PROCESSES

The invention relates to a composition for the oxidation dyeing of keratin fibers, containing a first oxidation base chosen from 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane, and the acid-addition salts thereof, at least one second selected oxidation base and at least one coupler; as well as to the oxidation dyeing process using this composition.

It is known practice to dye keratin fibers, and in particular human hair, with dye compositions containing oxidation dye precursors, in particular ortho- or para-phenylenediamines, ortho- or para-aminophenols, bis(phenyl)alkylenediamines or heterocyclic compounds, which are generally referred to as oxidation bases. Oxidation dye precursors, or oxidation bases, are colorless or weakly colored compounds which, when combined with oxidizing products, can give rise to colored and coloring compounds by a process of oxidative condensation.

It is also known that the shades obtained with these oxidation bases can be varied by combining them with couplers, *i.e.*, coloration modifiers. These couplers or coloration modifiers are chosen in particular from aromatic meta-diamines, meta-aminophenols, meta-diphenols and certain heterocyclic compounds.

The variety of molecules used as oxidation bases and couplers allows a wide variety of colors to be obtained.

The so-called "permanent" coloration obtained by means of these oxidation dyes should moreover satisfy a certain number of desired objectives. Thus, it is desired to

have no toxicological drawbacks, to obtain shades of the desired intensity and to show good resistance to external agents (light, bad weather, washing, permanent-waving, perspiration and friction).

The dyes should also allow grey hairs to be covered, and, lastly, they should be as unselective as possible, i.e. they should give the smallest possible differences in coloration along the same keratin fiber, which may in fact be differently sensitized (i.e. damaged) between its tip and its root.

It has already been proposed, in particular in patent application WO 92/13824, to use 2,5-diaminophenoxyoxaalkanes as oxidation bases and optionally in the presence of a coupler. However, the colorations obtained using these oxidation bases are not entirely satisfactory, in particular as regards the intensity of the colorations obtained and their resistance to the various treatments to which the hair may be subjected. The colorations obtained in particular show insufficient resistance to the action of light.

The inventor has now discovered, entirely surprisingly and unexpectedly, that the combination of 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane, and/or of at least one of the acid-addition salts thereof, with at least one second suitably selected oxidation base and at least one coupler, can give intense colorations which moreover can have improved properties of resistance with respect to the various attacking factors to which

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the hair may be subjected (shampooing, light, bad weather, permanent-waving, perspiration, friction, etc.).

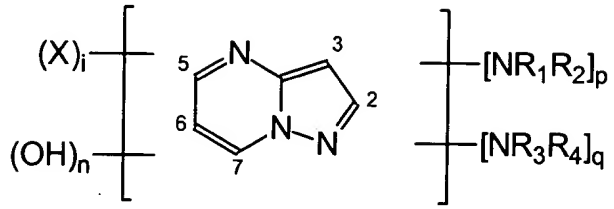
These discoveries form the basis of the present invention.

A first subject of the invention is thus a composition for the oxidation dyeing of keratin fibers, and in particular human keratin fibers such as the hair, comprising:

- at least one first oxidation base chosen from 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane and acid-addition salts thereof,

- at least one second oxidation base chosen from para-phenylenediamine, para-toluenediamine, N,N-bis-(β-hydroxyethyl)-para-phenylenediamine, 2-(β-hydroxyethyl)-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2-isopropyl-para-phenylenediamine, 2-chloro-para-phenylenediamine, N-phenyl-para-phenylenediamine, 4,4'-diaminodiphenylamine, N-methoxyethyl-para-phenylenediamine, 2-n-propyl-para-phenylenediamine, 4-aminophenol, N-methyl-4-aminophenol, 2-hydroxymethyl-4-aminophenol, 3-methyl-4-aminophenol, 2-aminomethyl-4-aminophenol, 2-(β-hydroxyethylaminomethyl)-4-aminophenol, 2-methoxy-4-aminophenol, 2-methoxymethyl-4-aminophenol, tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 4,5-diamino-1-ethyl-3-methylpyrazole, 4,5-diamino-N-methylpyrazole, 4,5-diamino-1-(4'-chlorobenzyl)pyrazole, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol, 3-amino-6-dimethylaminopyridine and

pyrazolo[1,5-a]pyrimidines of formula (I):



(I)

in which:

- R_1, R_2, R_3 and R_4, which are identical or different, are chosen from a hydrogen atom, C_1-C_4 alkyl radicals, aryl radicals, C_1-C_4 hydroxyalkyl radicals, C_2-C_4 polyhydroxyalkyl radicals, (C_1-C_4)alkoxy(C_1-C_4)alkyl radicals, C_1-C_4 aminoalkyl radicals wherein said amino can be protected with a protective group chosen from acetyl, ureido and sulphonyl groups, (C_1-C_4)alkylamino(C_1-C_4)alkyl radicals, di[(C_1-C_4)alkyl]amino(C_1-C_4)alkyl radicals, wherein said dialkyls can form a ring chosen from 5- and 6-membered aliphatic and heterocyclic rings, hydroxy(C_1-C_4)alkylamino(C_1-C_4)alkyl radicals, and di[hydroxy(C_1-C_4)alkyl]amino-(C_1-C_4)alkyl radicals;

- radicals X, are identical or different, and are chosen from a hydrogen atom, C_1-C_4 alkyl

radicals, aryl radicals, C_1-C_4 hydroxyalkyl radicals, C_2-C_4 polyhydroxyalkyl radicals, C_1-C_4 aminoalkyl radicals, (C_1-C_4)alkylamino(C_1-C_4)alkyl radicals, di[(C_1-C_4)alkyl]amino(C_1-C_4)alkyl radicals, wherein said dialkyls can form a ring chosen from 5- and 6-membered aliphatic and heterocyclic rings), hydroxy(C_1-C_4)alkyl- and di[hydroxy(C_1-C_4)alkyl]amino(C_1-C_4)alkyl radicals, amino radicals, (C_1-C_4)alkyl- and di[(C_1-C_4)alkyl]amino radicals; halogen atoms, carboxylic acid groups and sulphonic acid groups;

- i is chosen from 0, 1, 2 or 3;

- p is chosen from 0 or 1;

- q is chosen from 0 or 1;

- n is chosen from 0 or 1;

with the proviso that:

- (i) the sum p + q is other than 0;

- (ii) when p + q is equal to 2, then n is 0 and the groups NR_1R_2 and NR_3R_4 occupy positions (2,3); (5,6); (6,7); (3,5) or (3,7);

- (iii) when p is equal to 1 and q is equal to 0, then n is 1 and the group NR_1R_2 and the OH group occupy positions (2,3); (5,6); (6,7); (3,5) or (3,7);

- (iv) when p is equal to 0 and q is equal to 1, then n is 1 and the group NR_3R_4 and the OH group occupy positions (2,3); (5,6); (6,7); (3,5) or (3,7);

and acid-addition salts thereof;

- and at least one coupler.

As mentioned above, the dye composition in accordance with the invention can give intense colorations which moreover can have excellent properties of resistance with respect to the action of various external agents (light, bad weather, washing, permanent-waving, perspiration, friction). These properties can be particularly noteworthy as regards the light-fastness of the colorations obtained.

Representative pyrazolo[1,5-a]pyrimidines of formula (I), which can be used as the at least one second oxidation base in the dye compositions in accordance with the invention, include:

- pyrazolo[1,5-a]pyrimidine-3,7-diamine;
- 2-methylpyrazolo[1,5-a]pyrimidine-3,7-diamine;
- 2,5-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;
- pyrazolo[1,5-a]pyrimidine-3,5-diamine;
- 2,7-dimethylpyrazolo[1,5-a]pyrimidine-3,5-diamine;
- 3-aminopyrazolo[1,5-a]pyrimidin-7-ol;
- 3-amino-5-methylpyrazolo[1,5-a]pyrimidin-7-ol;
- 3-aminopyrazolo[1,5-a]pyrimidin-5-ol;
- 2-(3-aminopyrazolo[1,5-a]pyrimidin-7-ylamino)ethanol;

- 3-amino-7-β-hydroxyethylamino-5-methylpyrazolo[1,5-a]pyrimidine;

- 2-(7-aminopyrazolo[1,5-a]pyrimidin-3-ylamino)ethanol;

- 2-[(3-aminopyrazolo[1,5-a]pyrimidin-7-yl)-(2-hydroxyethyl)amino]ethanol;

- 2-[(7-aminopyrazolo[1,5-a]pyrimidin-3-yl)-(2-hydroxyethyl)amino]ethanol;

- 5,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;

- 2,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;

- 2, 5, N-7, N-7-tetramethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;

and acid-addition salts thereof.

The nature of the at least one coupler which can be used in the dye composition in accordance with the invention is not critical. They can be chosen from the couplers conventionally used for dyeing keratin fibers, such as meta-phenylenediamines, meta-aminophenols, meta-diphenols and heterocyclic couplers including, for example, indoles, indolines, pyridines, and pyrazolones, and acid-addition salts thereof.

Representative couplers include 5-amino-2-methylphenol, 5-N-(β-hydroxyethyl)amino-2-methylphenol, 3-aminophenol, 1,3-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 4-chloro-1,3-dihydroxybenzene, 2,4-diamino-1-(β-hydroxyethyloxy)benzene, 2-amino-4-(β-hydroxyethylamino)-1-methoxybenzene, 1,3-diaminobenzene, 1,3-bis(2,4-diaminophenoxy)propane, sesamol, α-naphthol, 6-hydroxyindole, 4-hydroxyindole, 4-hydroxy-N-methylindole, 6-hydroxyindoline,

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6-hydroxybenzomorpholine, 2,6-dihydroxy-4-methylpyridine, 1-H-3-methylpyrazol-5-one and 1-phenyl-3-methylpyrazol-5-one, and acid-addition salts thereof.

In general, representative acid addition salts used in the invention (oxidation bases and couplers) include hydrochlorides, hydrobromides, sulphates, citrates, succinates, tartrates, lactates and acetates.

The at least one first oxidation base chosen from 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane and acid-addition salts thereof preferably represent from 0.0005 to 12% by weight approximately relative to the total weight of the dye composition, and even more preferably from 0.005 to 6% by weight approximately relative to this weight.

The at least one second oxidation base in accordance with the invention and the acid-addition salts thereof preferably represent from 0.0005 to 12% by weight approximately relative to the total weight of the dye composition, and even more preferably from 0.005 to 6% by weight approximately relative to this weight.

The at least one coupler preferably represents from 0.0001 to 10% by weight approximately relative to the total weight of the dye composition, and even more preferably from 0.005 to 5% by weight approximately relative to this weight.

The medium which is suitable for dyeing (or support) generally comprises water or a mixture of water and at least one organic solvent to dissolve the compounds which would not be sufficiently water-soluble. As organic solvents, mention may be made, for

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example, of C_1-C_4 lower alkanols, such as ethanol and isopropanol; glycerol; glycols and glycol ethers such as 2-butoxyethanol, propylene glycol, propylene glycol monomethyl ether, diethylene glycol monoethyl ether and monomethyl ether, and aromatic alcohols such as benzyl alcohol or phenoxyethanol, similar products and mixtures thereof.

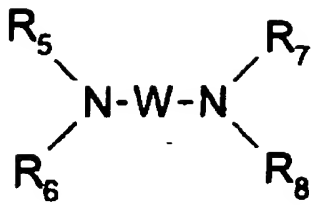
The solvents can be present in proportions preferably from 1 to 40% by weight approximately relative to the total weight of the dye composition, and even more preferably from 5 to 30% by weight approximately.

The pH of the dye composition in accordance with the invention is generally approximately from 3 to 12, and preferably approximately from 5 to 11. It can be adjusted to the desired value by means of acidifying or basifying agents usually used for dyeing keratin fibers.

Among the acidifying agents, mention may be made, for example, of inorganic or organic acids such as hydrochloric acid, orthophosphoric acid, sulphuric acid, carboxylic acids, such as acetic acid, tartaric acid, citric acid or lactic acid, and sulphonic acids.

Among the basifying agents, mention may be made, for example, of aqueous ammonia, alkaline carbonates, alkanolamines such as mono-, di- and triethanolamine and derivatives thereof, sodium hydroxide, potassium hydroxide and the compounds of

formula (II) below:



(II)

in which W is a propylene residue optionally having at least one substituent chosen from a hydroxyl group and C_1-C_6 alkyl radicals; R_5, R_6, R_7 and R_8, which may be identical or different, are chosen from a hydrogen atom and C_1-C_6 alkyl and C_1-C_6 hydroxyalkyl radicals.

The oxidation dye compositions in accordance with the invention can also contain at least one direct dye, in particular in order to modify the shades or to enrich them with glints.

The dye composition in accordance with the invention can also contain at least

one of various adjuvants conventionally used in compositions for dyeing the hair, such as anionic, cationic, nonionic, amphoteric or zwitterionic surfactants or mixtures thereof, anionic, cationic, nonionic, amphoteric or zwitterionic polymers or mixtures thereof, inorganic or organic thickeners, antioxidants, penetrating agents, sequestering agents, fragrances, buffers, dispersing agents, conditioners such as, for example, volatile or non-volatile, modified or unmodified silicones, film-forming agents, ceramides, preserving agents, sunscreens, and opacifiers.

Needless to say, a person skilled in the art will take care to select optional complementary compounds such that the advantageous properties intrinsically associated with the oxidation dye composition in accordance with the invention are not, or are not substantially, adversely affected by the addition(s) envisaged.

The dye composition according to the invention can be in various forms, such as in the form of liquids, creams, gels or any other form which is suitable for dyeing keratin fibers, and in particular human hair.

A subject of the invention is also a process for the oxidation dyeing of keratin fibers, and in particular human keratin fibers such as the hair, using the dye composition as defined above.

According to an embodiment of this process, at least one dye composition as defined above is applied to the fibers, the color being developed at acidic, neutral or

alkaline pH with the aid of an oxidizing agent which is added to the dye composition just at the time of use, or which is present in an oxidizing composition that is applied simultaneously or sequentially.

According to one preferred embodiment of the dyeing process of the invention, the dye composition described above is preferably mixed, at the time of use, with an oxidizing composition containing, in a medium which is suitable for dyeing, at least one oxidizing agent present in an amount which is sufficient to develop a coloration. The mixture obtained is then applied to the keratin fibers and is preferably left to stand on them for 3 to 50 minutes approximately, more preferably 5 to 30 minutes approximately, after which the fibers are rinsed, washed with shampoo, rinsed again and dried.

The oxidizing agent can be chosen from the oxidizing agents conventionally used for the oxidation dyeing of keratin fibers, such as hydrogen peroxide, urea peroxide, alkali metal bromates, persalts such as perborates and persulphates, and enzymes, among which mention may be made of peroxidases, 2-electron oxidoreductases such as uricases, and 4-electron oxygenases such as lactases. Hydrogen peroxide is particularly preferred.

The pH of the oxidizing composition containing the oxidizing agent as defined above is such that, after mixing with the dye composition, the pH of the resulting composition applied to the keratin fibers preferably ranges approximately from 3 to 12,

and even more preferably from 5 to 11. It is adjusted to the desired value using acidifying or basifying agents usually used for dyeing keratin fibers, such as those defined above. The oxidizing composition as defined above can also contain at least one adjuvant conventionally used in compositions for dyeing the hair and as defined above.

The composition which is finally applied to the keratin fibers can be in various forms, such as in the form of liquids, creams, gels or any other form which is suitable for dyeing keratin fibers, and in particular human hair.

Another subject of the invention is a multi-compartment dyeing device, *i.e*, "kit" or any other multi-compartment packaging system, a first compartment of which contains the dye composition as defined above and a second compartment of which contains the oxidizing composition as defined above. These devices can be equipped with a means for dispensing the desired mixture onto the hair, such as the devices described in patent FR-2,586,913 in the name of L'Oréal, the disclosure of which is specifically incorporated by reference herein.

The examples which follow are intended to illustrate the invention without, however, being limiting in nature.

EXAMPLES

EXAMPLES 1 to 6 OF DYEING IN ALKALINE MEDIUM

The dye compositions below, in accordance with the invention, were prepared (contents in grams):

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EXAMPLE	1	2	3	4	5	6
1,8-Bis(2,5-diaminophenoxy)-3,5-dioxaoctane tetrahydrochloride monohydrate	0.39	0.39	0.39	0.39	0.39	0.39
para-Phenylenediamine (second oxidation base)	0.162	-	0.162	-	-	-
para-Aminophenol (second oxidation base)	-	0.163	-	-	-	-
3-Methyl-4-aminophenol (second oxidation base)	-	-	-	0.184	-	-
2-(β-Hydroxyethyl)-para-phenylenediamine dihydrochloride (second oxidation base)	-	-	-	-	0.337	-
2,6-Dimethyl-para-phenylenediamine dihydrochloride (second oxidation base)	-	-	-	-	-	0.313
5-N-(β-Hydroxyethyl)amino-2-methylphenol (coupler)	0.498	-	-	-	-	-
2,4-Diaminophenoxyethanol dihydrochloride (coupler)	-	0.723	-	-	-	-
1,3-Dihydroxybenzene (coupler)	-	-	0.33	-	-	-
5-Amino-2-methylphenol (coupler)	-	-	-	0.369	-	-
3-Aminophenol	-	-	-	-	0.327	-
6-Hydroxybenzomorpholine						0.453

EXAMPLE	1	2	3	4	5	6
Common dye support No. 1	(*)	(*)	(*)	(*)	(*)	(*)
Demineralized water qs	100 g	100 g	100 g	100 g	100 g	100 g

(*) Common dye support No. 1:

- 96° Ethyl alcohol	18 g
- Sodium metabisulphite as an aqueous solution at 35%	0.68 g
- Pentasodium salt of diethylenetriamine-pentaacetic acid	1.1 g
- Aqueous ammonia containing 20% NH_3	10.0 g

Each of the above dye compositions was mixed weight for weight, at the time of use, with a 20-volumes hydrogen peroxide solution (6% by weight) of pH 3.

The mixture obtained was applied to locks of natural permanent-waved grey hair containing 90% white hairs, for 30 minutes. The locks were then rinsed, washed with a standard shampoo, rinsed again and then dried.

The shades obtained are given in the table below:

EXAMPLE	Dyeing pH	Shade obtained on natural hair	Shade obtained on permanent-waved hair
1	10±0.2	Violet iridescent light chestnut	Violet chestnut
2	10±0.2	Violet-ash	Strong blue
3	10±0.2	Iridescent golden dark blond	Iridescent golden light chestnut
4	10±0.2	Violet iridescent blond	Ash-violet light chestnut
5	10±0.2	Grey	Strong matt-grey
6	10±0.2	Golden green	Light green

EXAMPLES 7 TO 12 OF DYEING IN NEUTRAL MEDIUM

The dye compositions below, in accordance with the invention, were prepared (contents in grams):

EXAMPLE	7	8	9	10	11	12
1,8-Bis(2,5-diaminophenoxy)-3,5-dioxaoctane tetrahydrochloride monohydrate	0.39	0.39	0.39	0.39	0.39	0.39
para-Phenylenediamine (second oxidation base)	0.162	-	0.162	-	-	-
para-Aminophenol (second oxidation base)	-	0.163	-	-	-	-
3-Methyl-4-aminophenol (second oxidation base)	-	-	-	0.184	-	-
2-(β-Hydroxyethyl)-para-phenylenediamine dihydrochloride (second oxidation base)	-	-	-	-	0.337	-
2,6-Dimethyl-para-phenylenediamine dihydrochloride (second oxidation base)	-	-	-	-	-	0.313
5-N-(β-Hydroxyethyl)amino-2-methylphenol (coupler)	0.498	-	-	-	-	-
2,4-Diaminophenoxyethanol dihydrochloride (coupler)	-	0.723	-	-	-	-
1,3-Dihydroxybenzene (coupler)	-	-	0.33	-	-	-
5-Amino-2-methylphenol (coupler)	-	-	-	0.369	-	-
3-Aminophenol	-	-	-	-	0.327	-
6-Hydroxybenzomorpholine						0.453

EXAMPLE	7	8	9	10	11	12
Common dye support No. 2	(**)	(**)	(**)	(**)	(**)	(**)
Demineralized water qs	100 g	100 g	100 g	100 g	100 g	100 g

(**) Common dye support No. 2:

- 96° Ethanol	18 g
- K_2HPO_4/KH_2PO_4 (1.5M/1M) buffer	10 g
- Sodium metabisulphite	0.68 g
- Pentasodium salt of diethylenetriamine-pentaacetic acid	1.1 g

Each of the above dye compositions was mixed weight for weight, at the time of use, with a 20-volumes hydrogen peroxide solution (6% by weight) of pH 3.

The mixture obtained was applied to locks of natural or permanent-waved grey hair containing 90% white hairs, for 30 minutes. The locks were then rinsed, washed with a standard shampoo, rinsed again and then dried.

The shades obtained are given in the table below:

EXAMPLE	Dyeing pH	Shade obtained on natural hair	Shade obtained on permanent-waved hair
7	5.7±0.2	Violet light-chestnut	Strong violet-chestnut
8	5.7±0.2	Ashen dark-bond	Strong ashen light chestnut
9	5.7±0.2	Strong ash-grey	Strong grey
10	5.7±0.2	Ash-grey	Violet ash-grey

EXAMPLE	Dyeing pH	Shade obtained on natural hair	Shade obtained on permanent-waved hair
11	5.7±0.2	Blue-grey	Blue-grey
12	5.7±0.2	Golden green	Green

While the invention has been described in terms of various preferred embodiments and specific examples, those skilled in the art will recognize that various changes and modifications can be made without departing from the spirit and scope of the invention, as defined in the appended claims.